SCANNING ELECTRON MICROSCOPY OF THE EPIGENETIC MINERALS AT PUGH QUARRY, WOOD COUNTY, OHIO

Presented in partial fulfillment of the requirements
for the degree of Bachelor of Science in the
Department of Geology and Mineralogy
of THE OHIO STATE UNIVERSITY

Betsy J. Dransfield

1980

Approved by ______________________

Advisor

TABLE OF CONTENTS

ACKNOWLEDGMENTS

I wish to express my thanks to my advisor, Dr. Douglas E. Pride, who suggested this topic and provided a great deal of helpful advice. Thanks also go to Dr. Dan McLachlan, Jr. and Dr. Henry E. Wenden for their willing discussions of problems in crystal morphology. I would like to thank the Friends of Orton Hall fund for financial support in performing SEM studies.

INTRODUCTION

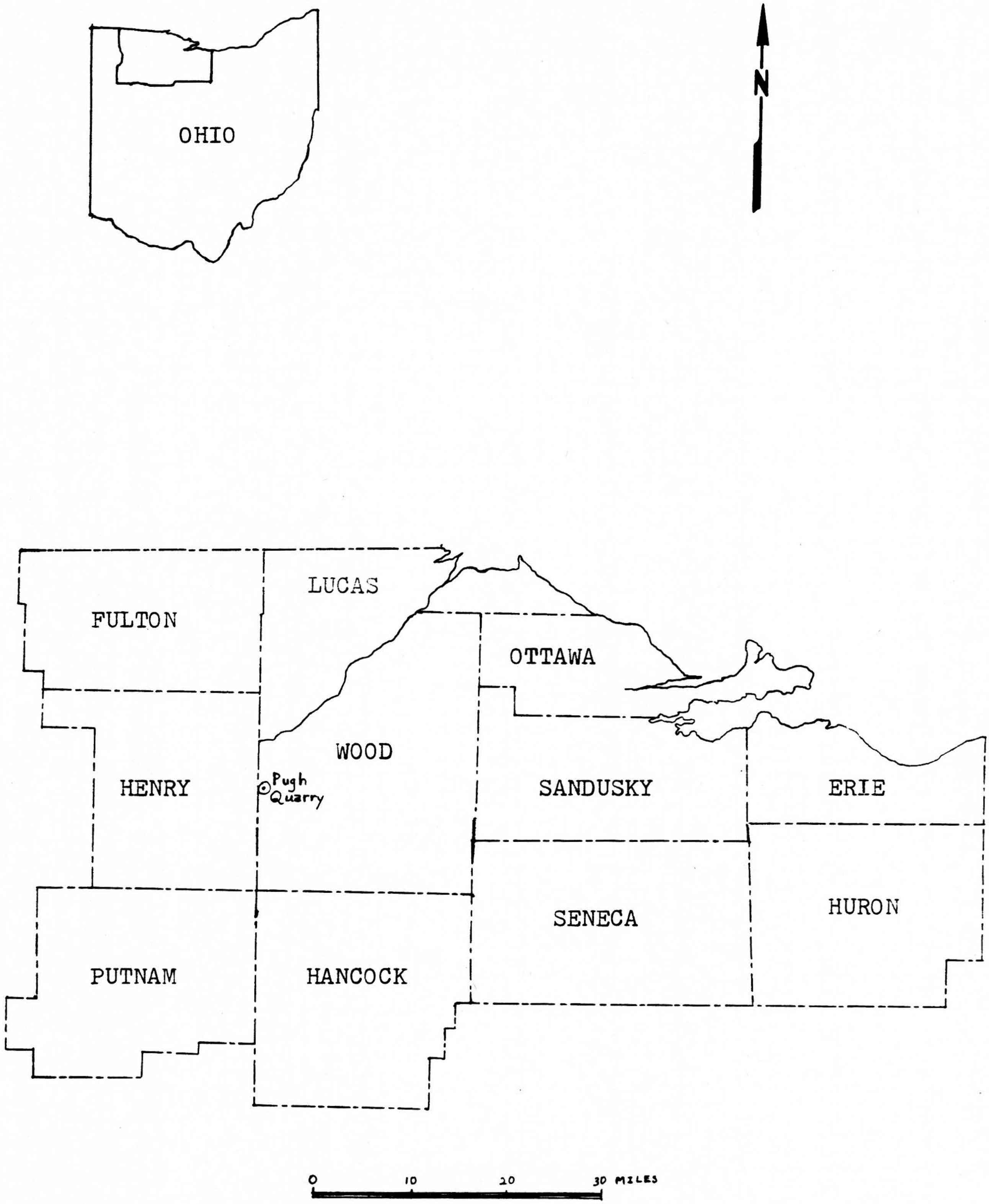
The Pugh Stone Quarry, situated in southwestern Wood County, is one of many locations in northwestern Ohio in which cavities in dolomite and limestone are lined with secondary minerals. Epigenetic minerals found at Pugh Quarry include sphalerite, fluorite, barite, celestite, marcasite, pyrite, and calcite.

The purpose of this report was to study the small-scale characteristics of the epigenetic minerals using the scanning electron microscope(SEM), noting mineral associations, and describing mineral growth.

PREVIOUS WORK

The stratigraphy of the Devonian sequences in northwestern Ohio has been described by numerous geologists, including Carman (1927), Stout (1941), and Janssens (1968). Chapel (1975) compiled a descriptive and interpretive analysis of the Devonian carbonates in Ohio, including specific stratigraphic data on Pugh Quarry.

The descriptive mineralogy of Pugh Quarry has been studied in detail by Parr and Chang (1977,1978,1979,1980). These workers described physical characteristics of crystals using low-power microscopy and goniometric measurements, as well as mineral associations and host rock relationships of all of the epigenetic minerals found



APPROXIMATE GEOGRAPHICAL LOCATION OF PUGH QUARRY within the quarry. Their work included thin section, polished section, and hand specimen studies.

High quality, high resolution SEM characterization of epigenetic mineralization, with respect to mineral-to-host rock and mineral-to-mineral associations, was not found.

STRATIGRAPHY

Devonian formations found at Pugh Quarry include the Sylvania Sandstone, the Detroit River Dolomite, and the Dundee Limestone (Chapel, 1975). The Sylvania Sandstone, exposed only in the quarry sump, consists primarily of cross-bedded and ripple-marked sandstone and fossiliferous sandy dolostone. Gypsiferous mudstone of the basal Detroit River overlies the Sylvania Sandstone.

The Detroit River, at other locations, has been divided into the Amherstburg Dolomite, the Lucas Dolomite, and the Anderdon Limestone members. The Lucas Dolomite is the only member present at Pugh Quarry. It consists of 55 feet of laminated calcareous mudstone with some algal stromatolitic limestone (Chapel, 1975). The upper portion of the Lucas Dolomite includes recrystallized oolitic calcarenite. Beds of breccia containing fragments of dolostone occur throughout the Lucas Dolomite. Cavities within the breccia beds are the principal locations for secondary mineralization which includes sphalerite, barite, fluorite, celestite, marcasite, and calcite.

The "lower Dundee" overlies the Detroit River and consists of 28 feet of massive light tan to dark brown color-banded porous dolostone. Dolomite crystals generally are dark-centered with clear rims. Color contacts often are burrowed, and upper units have relict laminations (Chapel, 1975).

FIELD WORK AND LABORATORY PROCEDURES

Samples for study were collected in 1975 by Dr. Douglas E. Pride of the Ohio State University. Thin sections were prepared by cutting 20mm by 40mm chips from ten of the samples. The chips were ground down to 600 carborundum on grinding wheels, then mounted on glass slides with Hilquist epoxy. The mounted chips were cut with a thin section saw and taken down to approximately 30 microns with a thin section grinder. A final grinding was given by hand, using 600 carborundum and a glass plate. Thin sections were then covered.

Samples to be studied with the SEM were prepared by cutting chips averaging 8mm by 8mm by 5mm with the diamond rock saw. The surface to be mounted on the SEM stub was ground with 200 carborundum on a grinding wheel. Samples were stored in a dessicator overnight and mounted with graphite cement. To enhance conductivity, the samples were coated with fine layers of carbon and gold in a vacuum evaporator. The scanning electron microscope used is a Cambridge model S4-10.

RESULTS

Thin Section and Hand Specimen Studies

Study of the thin sections revealed that the host rock for the epigenetic mineralization is mostly dolomitized limestone. The samples in which fluorite predominates (Samples PQ-2, PQ-3 PQ-4) are very fine-grained, light gray dolostones, characterized by alternating light and dark wavy bands which suggest an algal stromatolite origin. The fluorite crystallized in vugs of 2-40mm in diameter. Sample PQ-3 contains minute amounts of gypsum in addition to fluorite.

Sphalerite, marcasite, and pyrite are abundant in light gray porous dolostone (Samples PQ-1, PQ-9). Marcasite and calcite also are present as encrustations on recrystallized oolitic grainstone (PQ-8) and on highly fractured fine-grained dolostone (PQ-7). In both cases, calcite crystals generally coat the marcasite.

The remaining samples (PQ-5, PQ-6, PQ-10) exhibit evidence of carbonate diagenesis by neomorphism and void-filling, but little fluorite or sulfide mineralization.

Scanning Electron Microscopy

The SEM study deals with specimens of the following four minerals: sphalerite, marcasite, fluorite, and calcite.

Sphalerite-occurs macroscopically with marcasite, pyrite, calcite, and fluorite. Sphalerite crystals examined range from 0.5-1.0mm in diameter and occur in rounded aggregates of subhedral to euhedral crystals. The most common crystal form exhibited is a malformed dodecahedron in which some of the crystal faces are curved (Fig. 1). Many crystal faces also show striations indicative of polysynthetic twinning. Deep surface pits (Fig. 2) probably represent plucking of small crystals from the surfaces of the sphalerite. Euhedral fluorite cubes from .003-.007mm in diameter were observed with sphalerite in Figure 2. Euhedral calcite rhombohedrons ranging from .009-.012mm in diameter also were found on the surfaces and within depressions in the sphalerite (Figs. 2 and 3).

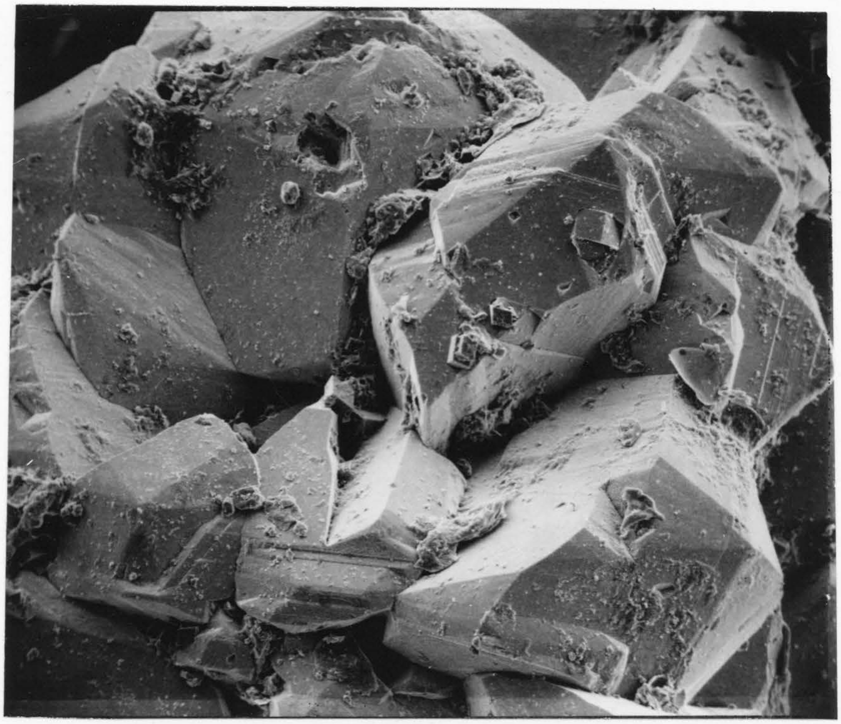


Figure 1. Striated sphalerite dodecahedrons
on dolostone.
(260X)

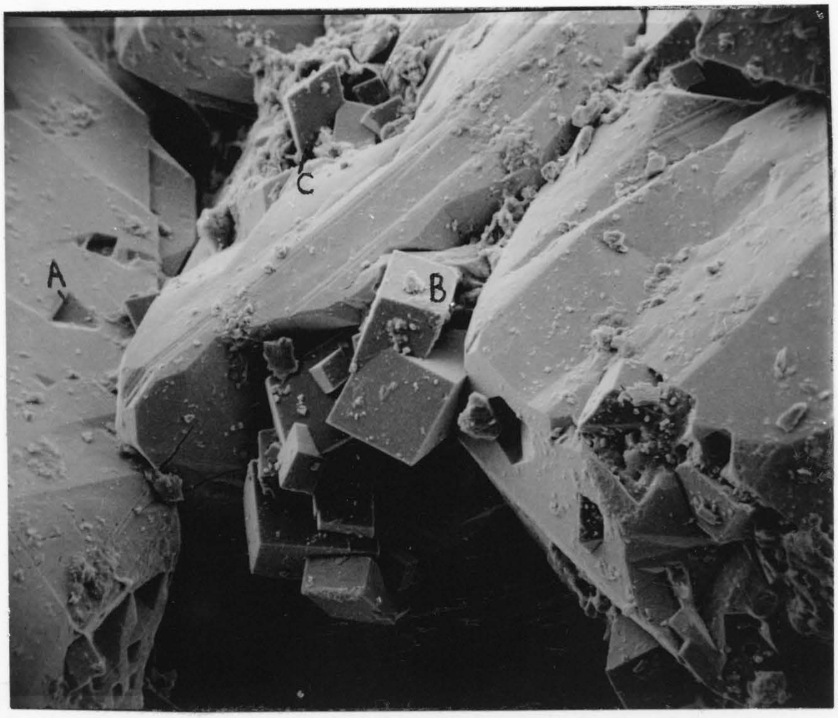


Figure 2. A) Surface depressions on sphalerite
B) Fluorite cubes on sphalerite
C) Calcite rhombohedrons in sphalerite depressions
(570X)

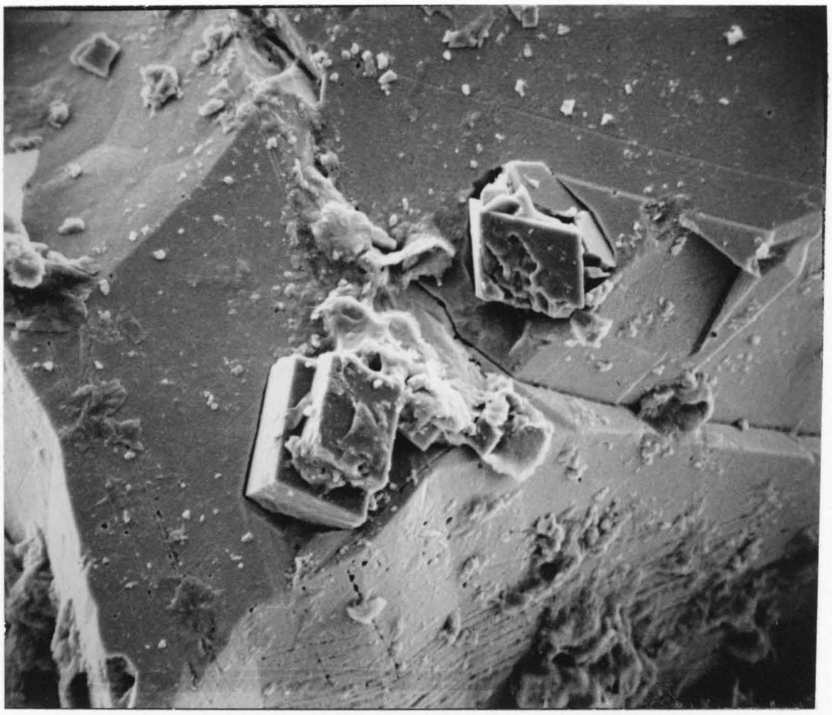


Figure 3. Calcite rhombohedrons on sphalerite (1120X)

<u>Marcasite and pyrite</u>- occur primarily with calcite as encrustations on dolostone. Although pyrite dodecahedrons are visible, tabular marcasite crystals are far more common (Figs. 4 and 5). Crystals of both pyrite and marcasite are euhedral and range from 0.3-0.5mm in diameter. Most crystal faces are flat and smooth, with little pitting. Smaller crystals of marcasite apparently began to grow on some of the faces prior to the cessation of mineralization (Fig. 6). Figure 7 exhibits small calcite crystals (.004-.023mm in diameter) forming on and growing out of marcasite surfaces.

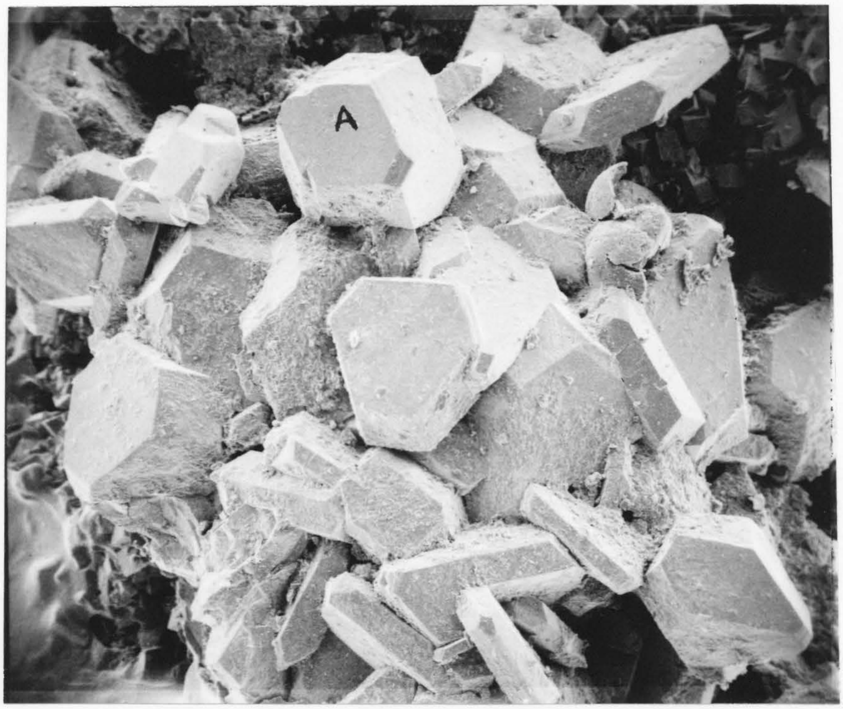


Figure 4. Marcasite and pyrite on dolostone. Note pyrite dodecahedron (A). (60X)

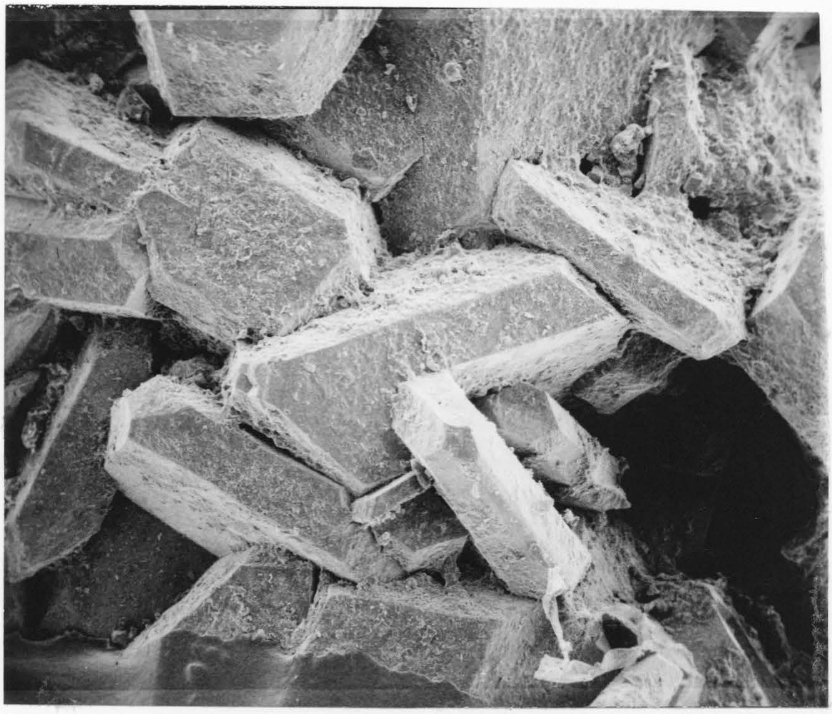


Figure 5. Marcasite crystals exhibiting tabular habit. (110X)

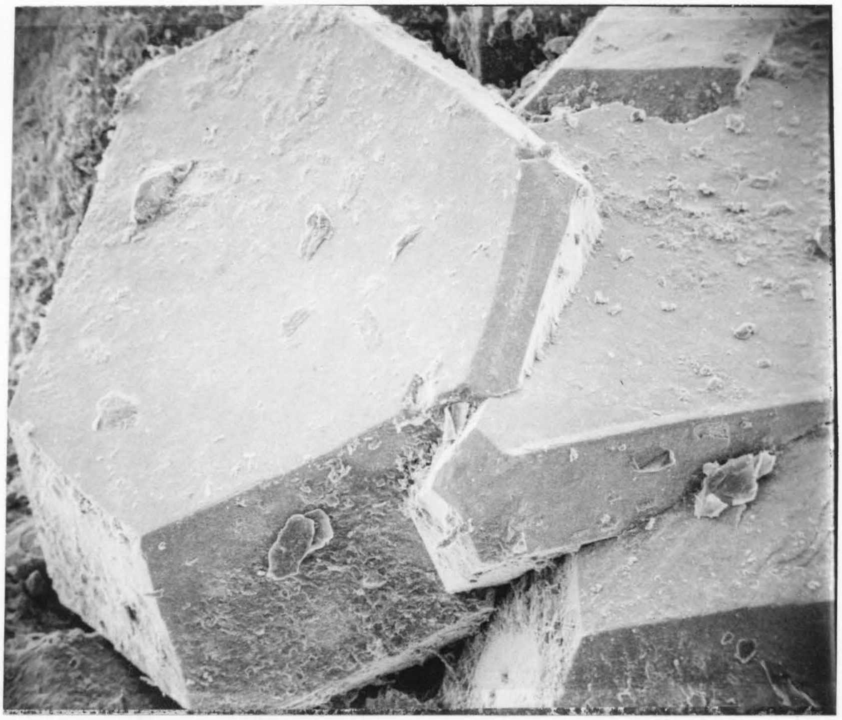


Figure 6. Small marcasite crystals on marcasite surface.
(225X)

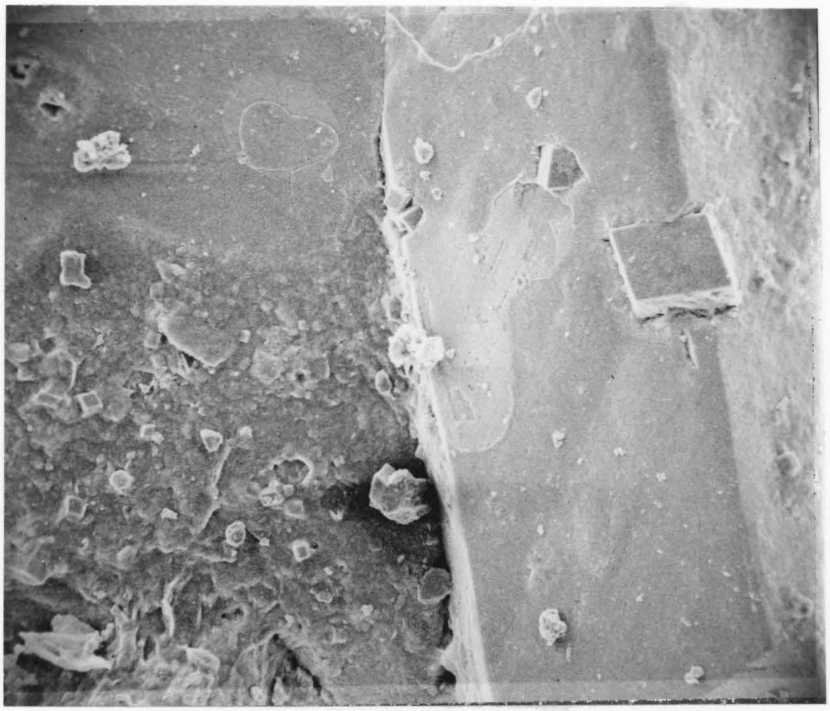


Figure 7. Calcite rhombohedrons on marcasite.
(570X)

Fluorite- aggregates occur with marcasite and sphalerite within the dolostone host rock. Euhedral cubes of fluorite ranging from .60-1.70mm in diameter exhibit distinct edges and generally smooth, flat faces (Fig. 8). Some crystal faces exhibit imperfections, but little mineralization other than minute fluorite crystals was observed.

The large fluorite crystals exhibit layered surface features of questionable origin (Fig. 8,A&B). The steps probably resulted from either the collapse of a growth spiral produced by a screw dislocation (Azaroff, 1960) or the successive formation of new nuclei on the crystal surface. Indentations exhibited on crystal faces in Figures 9 and 10 were difficult to classify, but may represent "hopper" crystal growth, indicating relatively rapid crystal growth (D. McLachlan, personal communication, 1980), or plucking of some foreign crystal from the fluorite surface. The cleavage angles in Figure 9 suggest a possible origin of skeletal growth as hexoctahedral striations on the cube face (H. Wenden, personal communication, 1980). However, interruptions in the striations suggest a fracture surface. The surface depression in Figure 10 opposes cleavage directions, suggesting that plucking probably occurred. Most of the large fluorite crystals penetrate other cubes, but penetration twinning was not found.

Small fluorite crystals (.02-.22mm in diameter) are visible on surfaces of the larger cubes (Fig. 11). In addition, a few rhombohedrons of calcite are noticeable at and above magnifications of 200X (Fig. 12).

Figure 8. Fluorite cubes on dolostone. Note surface layers at A and B.
(20X)

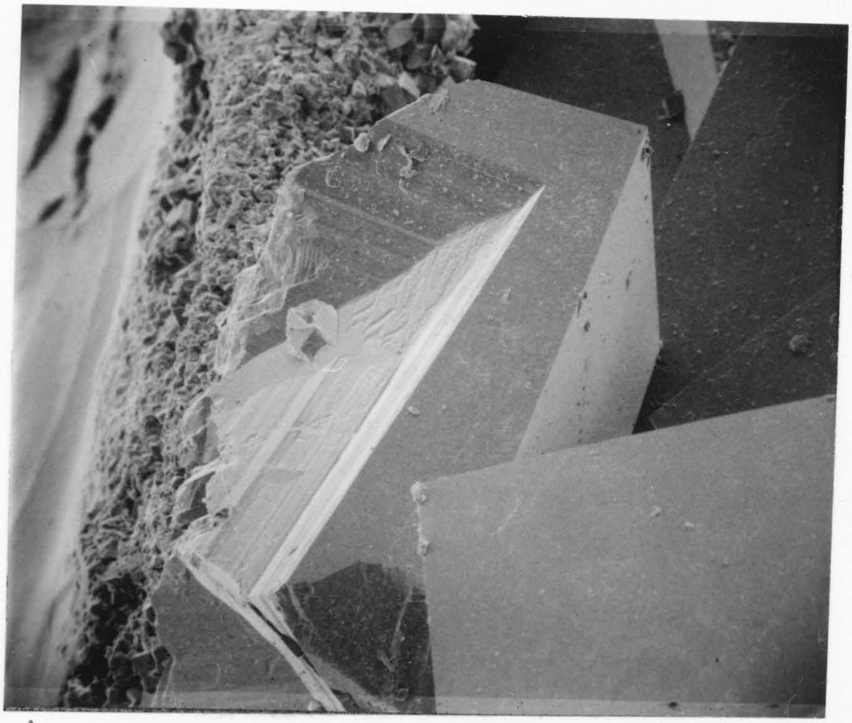
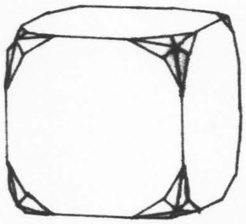


Figure 9. Striated surface depression in fluorite cube.



Fluorite hexoctahedron on the cube (Dana, 1977).

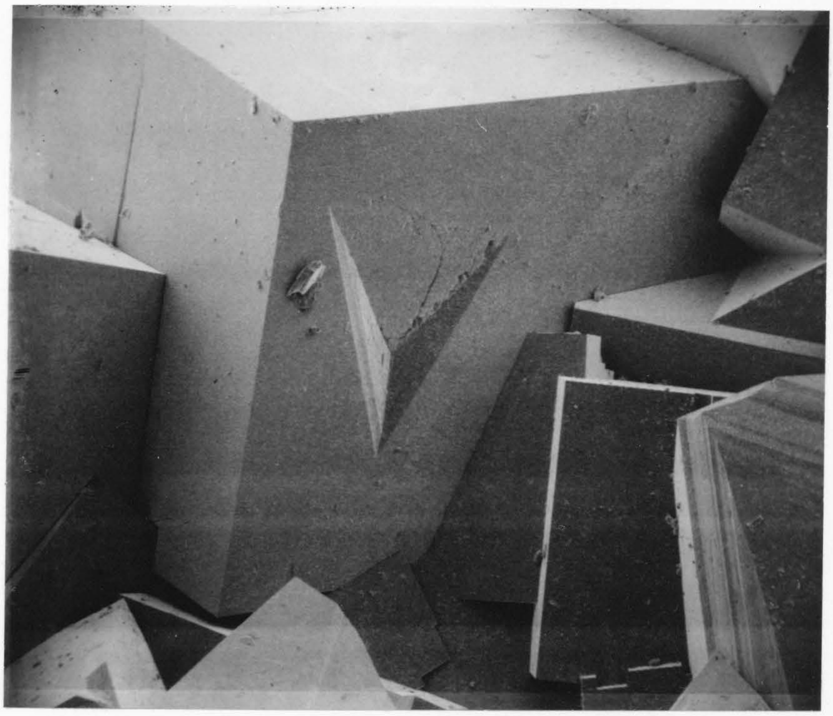


Figure 10. Surface indentation in fluorite cube face.
(60X)

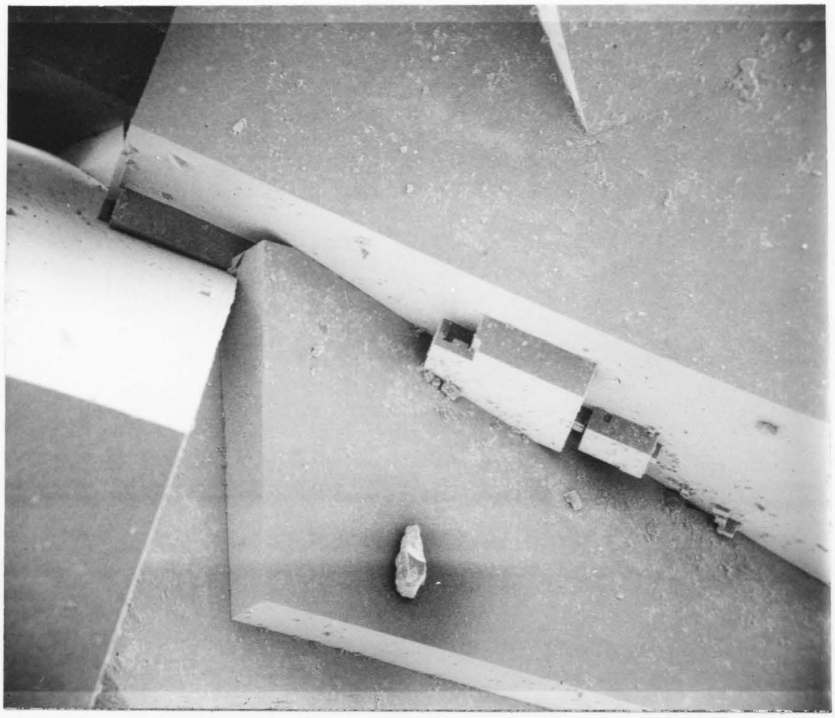


Figure 11. Small fluorite crystals on fluorite cubes.
(110X)

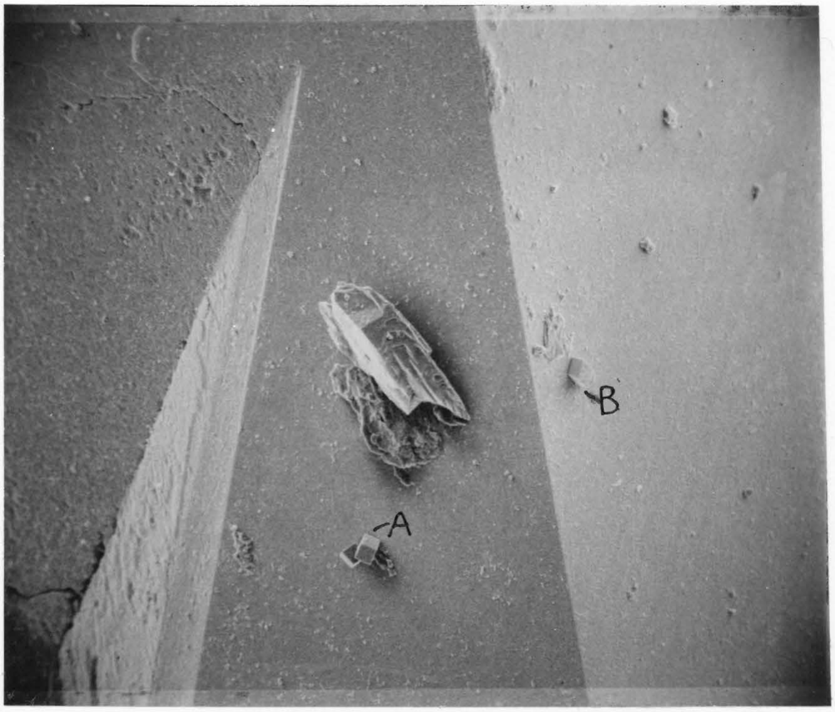


Figure 12. Calcite crystals (A & B) on fluorite. (230X)

<u>Calcite</u>- crystals studied are euhedral scalenohedrons (dogtooth) ranging from .44-1.74mm in diameter, exhibiting curved faces and some pitting (Fig. 13). Cavities within the calcite crystals range from .005-.033mm in diameter and contain calcite rhombs and barite clusters (Figs. 14, 15, and 16). The barite appears as radiating oblong crystal aggregates. According to Parr and Chang (1980), barite also encrusts portions of larger calcite crystals. Minor encrustations of tabular barite upon calcite were observed in some specimens (Fig. 17).

Many of the calcite surfaces exhibit fracturing, leaving the characteristic cleavage traces (Figs. 18-20). The fracture surface shown in Figures 18 and 19 suggests that the calcite crystal was broken partially along cleavage, and then etched by later solutions migrating through the rock. The small crystals of calcite (Fig. 20,A & B) probably originated by reprecipitation of calcium carbonate from the same solutions.

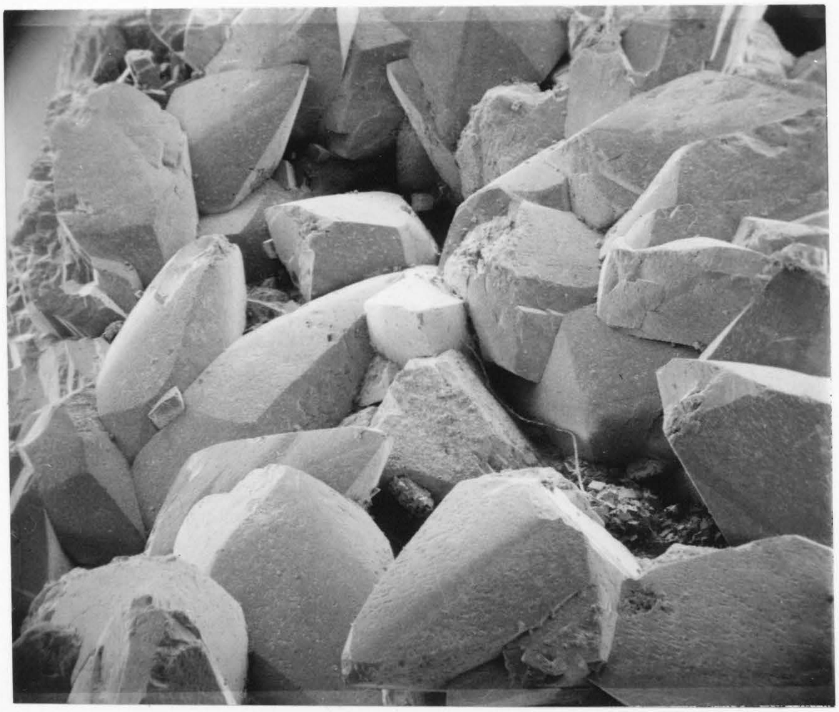


Figure 13. Calcite scalenohedrons on dolostone.
(20X)

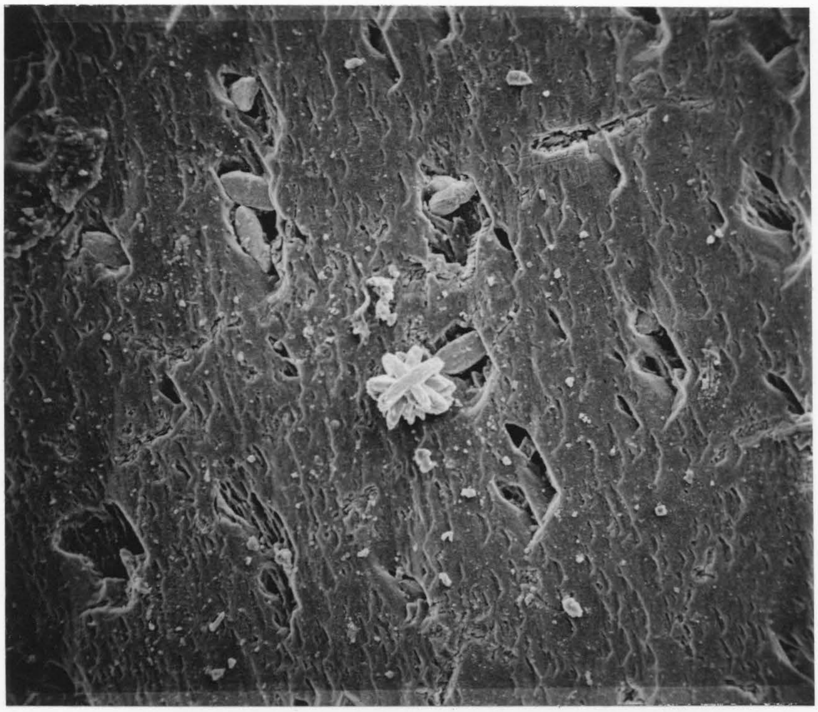


Figure 14. Cluster of radiating barite crystals on calcite crystal.
(610X)

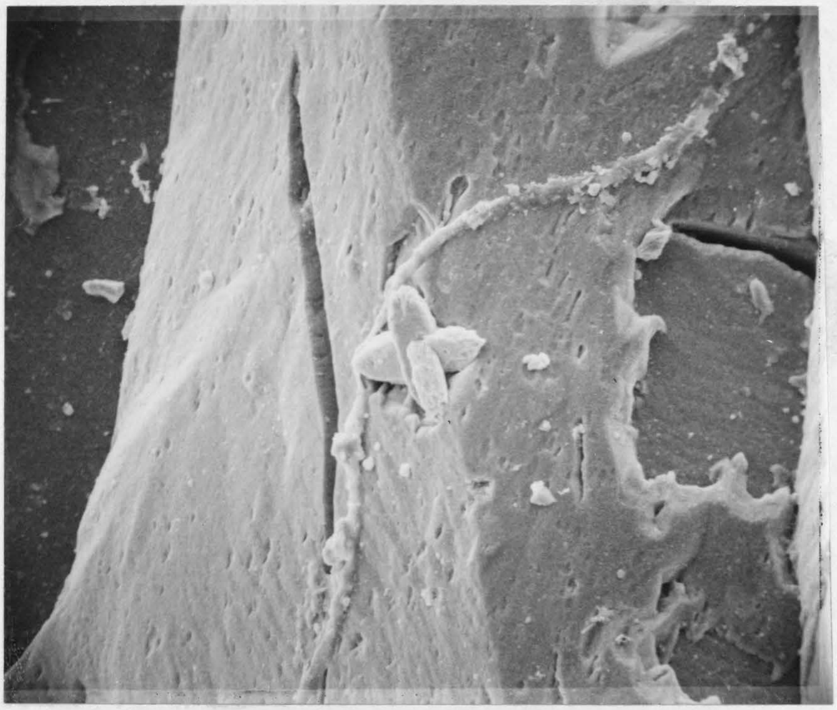


Figure 15. Cluster of radiating barite crystals within cavity of calcite scalenohedron. (1100X)

Figure 16. Small calcite rhombohedrons on large calcite crystals. (610X)

Figure 17. Tabular barite encrusting calcite crystal surface.
(240X)

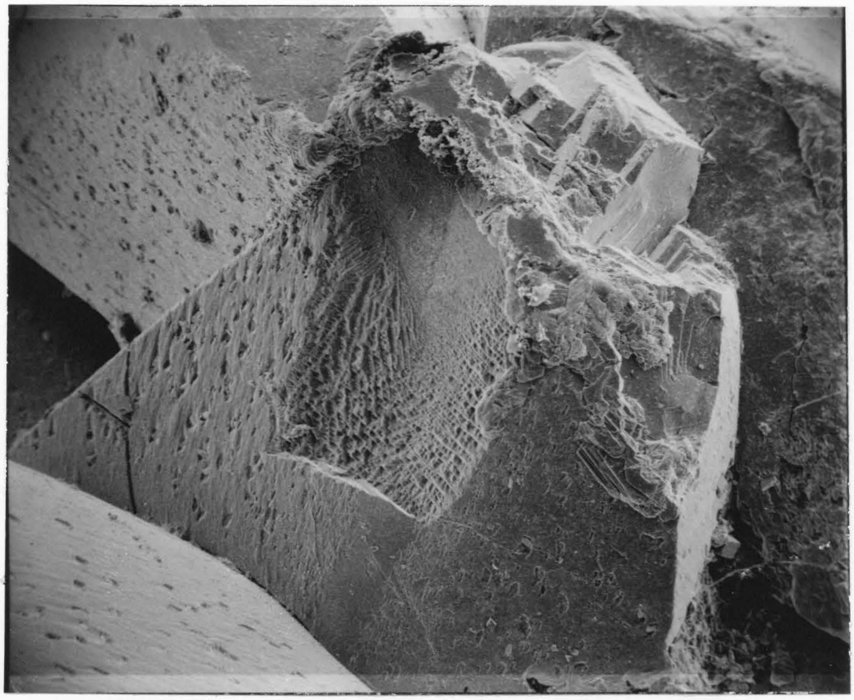


Figure 18. Calcite scalenohedron exhibiting fracture surface.
(120X)

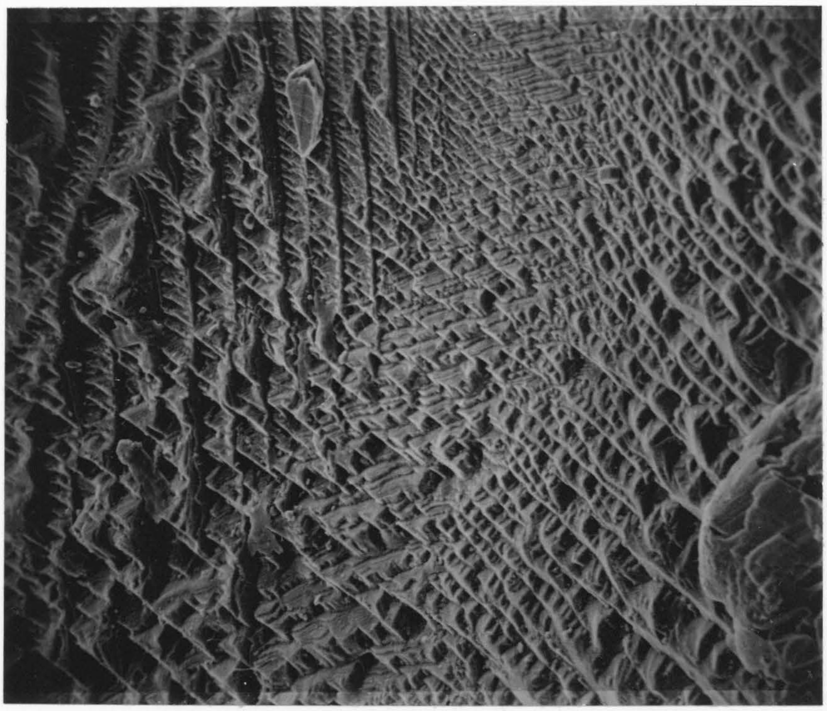


Figure 19. Fracture surface in Figure 18 enlarged to show cleavage, fracture, and etching features.
(590X)

Figure 20. Fracture surface exhibiting one direction of cleavage and fracture features. Note small calcite rhombohedrons (A & B). (550X)

DISCUSSION

Fluids migrating through the carbonate host rocks of the Pugh Quarry carried iron, zinc, fluorine, sulfur, magnesium, and calcium, with minor amounts of barium and strontium. The secondary mineralization is characterized by large subhedral to euhedral crystals, suggesting that there was ample time for crystallization. Growth was not obstructed by surrounding host rock. Sphalerite crystallization began but had not ended before fluorite began to crystallize. It was not possible to determine the order of marcasite/pyrite formation with respect to sphalerite and fluorite. Large calcite crystals (1.0-8.0mm in diameter) were observed on marcasite encrustations in thin section, indicating that calcite formed after the marcasite. In addition, smaller calcite crystals, on the order of .005mm in diameter, were observed on all of the epigenetic mineral phases, including barite encrustations. The small calcite crystals resulted either from a late stage of mineralization or from a continuation of the mineralization producing the larger calcite crystals.

REFERENCES CITED

Azaroff, L.V.(1960), Introduction to Solids, McGraw-Hill Book Company, Inc., p.153.

Carman, J.E.(1927), "The Monroe Division of Rocks in Ohio," Jour. Geol., Vol.35, no.6, pp.481-506..

Chapel, J.D.(1975), Petrology and Depositional History of Devonian Carbonates in Ohio, Unpublished Doctoral Dissertation, OHIO STATE UNIVERSITY.

Dana, J.D., Manual of Mineralogy, 19th Ed. (after J.D. Dana), John Wiley & Sons, Inc., 1977, p.292.

McLachlan, D., Personal Communication, May 1980.

Parr, D.F. and L.L.Y. Chang(1980), "Descriptive Mineralogy of Pugh Quarry, Northwestern Ohio: Barite and Celestite," Ohio J. Sci., vol.80, no.1, pp.20-29.

Stout, W.(1941), "Dolomites and Limestones of Western Ohio," Geological Survey of Ohio, Fourth Series, Bulletin 42, pp.383-395.

Wenden, H.E., Personal Communication, May, 1980.